COMPACT MEMBRANE SYSTEMS, INC.

Final Report

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1. Project Objective:

There are many industrial catalytic organic reversible reactions with amines or alcohols that have water as one of the products. Many of these reactions are homogeneously catalyzed. In all cases removal of water facilitates the reaction and produces more of the desired chemical product. By shifting the reaction to right we produce more chemical product with little or no additional capital investment. Many of these reactions can also relate to bioprocesses. Given the large number of water-organic compound separations achievable and the ability of the Compact Membrane Systems, Inc. (CMS) perfluoro membranes to withstand these harsh operating conditions, this is an ideal demonstration system for the water-of-reaction removal using a membrane reactor. Enhanced reaction synthesis is consistent with the DOE objective to lower the energy intensity of U.S. industry 25% by 2017 in accord with the *Energy Policy Act of 2005* and

to improve the United States manufacturing competitiveness. The objective of this program is to develop the platform technology for enhancing homogeneous catalytic chemical syntheses.

2. Background:

A major structural change is needed in the U.S. Chemical Industry to compete globally, and to reduce the impact of future increases in energy costs. In particular, new technologies are needed that can significantly reduce energy costs in large volume categories of chemical products, not just achieve incremental savings in energy usage. A structural reduction in energy consumption for specific large volume chemical products would not only offer a strategic competitive advantage to U.S. industry, but also would inherently reduce carbon dioxide emissions and associated global warming risks. The benefits which would accrue from such radical new technologies include increased productivity, economic competitiveness, and employment. The present program addressed this need.

Compact Membrane Systems (CMS) has developed nonporous high gas flux membranes. This perfluoro system has temperature ratings as high as 190°C. With this high temperature rating and excellent chemical resistance, it has universal applicability, in most organic-water environments, for potential separation of the water produced from reactions of interest. Given the large number of water-organic compound separations achievable and the ability of the perfluoro membranes to withstand these harsh operating conditions, this is an ideal system for the water-of-reaction removal using a membrane reactor.

Problem/Opportunity: Many catalytic organic reversible reactions with amines or alcohols have water (H₂O) as a common product of reaction (see Table 1). Many of these reactions are homogeneously catalyzed. In all cases removal of water shifts the reaction to the right which produces more product. By shifting the reaction to right we produce more product with little or no additional capital investment. Many of these reactions relate to bioprocesses. This program will develop platform technology enhancing homogeneous catalytic and/or biocatalytic processes. Therefore we are responsive to the integrated reactor technology of the opportunity.

Table 1. Reversible Organic Reactions			
Reactant A	Reactant B	Product Type	Example
Acid	Alcohol	Ester	C ₆ H ₅ OOC ₆ H ₅
Acid	2 Alcohols	Orthoester	CH ₃ C(OC ₂ H ₅) ₃
Aldehyde	Alcohol	Ether	CH ₃ CH ₂ CH ₂ (OC ₂ H ₅)
Ketone	Alcohol	Ketal	CH ₃ CH ₂ CH(OC ₂ H ₅) ₂
Aldehyde or Ketone	Amine	Imine	CH ₃ CH=NH

The diversity of the acids, aldehydes, ketones, alcohols and amines, that is, straight chain, ring and other attached R groups result in a multitude of products such as polymers, pharmaceuticals, surfactants, fungicides, insecticides, and biologically active compounds. The formation of the desired product requires removal of the water of reaction. Removal technologies range from boiling to more complex separations such as azeotropic distillation with a solvent. In every case the removal of the water requires large amounts of energy for direct heating, regeneration of any solvent or dehydrating agent, storage, heating and transfer of the solvent, and treatment of the generated waste.

Removal of water from equilibrium limited reaction mixture $A + B \rightleftharpoons C + H_2O$ shifts reaction to the right. If excess cheaper reactant (say A) is used, full conversion of the more expensive reactant (say B) can be realized. This results in higher yield of desired product and thereby lower

reagent consumption. Further, the desired product has no longer to be separated and purified from a four component mixture (two reactants A and B, product C and water), but from a two component mixture. When water is removed by the pervaporation membrane and one of the reagents (B) is nearly totally converted, the product C has to be separated and purified from the surplus reactant A only. This facilitated downstream purification may be economically as important as the higher yield and conversion. Therefore, removal of co-product water reduces production costs three ways: higher yield, faster reaction and purer products. While reactive distillation can be used, it is limited to volatility differences. By contrast the CMS membrane technology is viable for any reaction where water is generated. Enhanced reaction synthesis is consistent with the DOE objective to lower the energy intensity of U.S. industry 25% by 2017 in accord with the *Energy Policy Act of 2005* and to improve the United States manufacturing competitiveness.

Product Concept – Technical Approach: Compact Membrane Systems uses a nonporous high flux perfluoro membrane (CMS-3 or CMS-7) on a microporous support in a perfluoro shell with perfluoro potting. This perfluoro system has temperature ratings as high as 130°C. With the high temperature rating and excellent chemical resistance, this system has universal applicability in almost any organic-water environment for potential separation of the reaction water for the reactions listed in Table 1. Given the large water-organic compound separations achievable and the ability to withstand these harsh operating conditions (e.g., 125°C in propionic acid), we believe this is the ideal system for the water-of-reaction removal in a membrane reactor.

The separation characteristic of the membrane reactor, that is rapidly removing water, not only favors an equilibrium reaction, but also is more energy efficient. A conventional reactor system requires a separation device to separate the products from any unreacted feeds and to separate the two products from each other. With a membrane reactor and its rapid removal of water the separation of feeds from the product will be a smaller device, and the separation of the two reaction products is no longer necessary.^{1,2} This saves energy as well as increases reaction rate.

Innovation: A membrane reactor is defined as a membrane process/device that performs net chemical conversions by exploiting its unique contacting features, that is the ability to organize, compartmentalize, and/or separate.^{1,2} Membrane reactors can combine several processing operations at once, such as reaction and purification. For a reversible reaction the separation of a product through a semipermeable membrane affects the extent and rate of reaction. For example the reversible reaction:

As either R or S permeates through the membrane the reaction is forced towards the products and the reverse reaction term in the rate equation becomes smaller.

The mechanical passive separation of the product and water during reaction would result in a more complete reaction, fewer non-value materials being added to the process, and significant savings in energy usage. The large ranges of products listed in Table 1 preclude using single membrane reactors that would remove the product. In fact most of the products are molecules

¹ Ho, W. W. and Sirkar, K., *Membrane Handbook*, Chapman & Hall, 1992, Chapter 43

² Sirkar, K. K. et al., "Membrane in a Reactor: A Functional Perspective.", *Ind. Eng. Chem. Res.*, Vol.38, No. 10, 1999, pp.3715-3737

either too large or not soluble in membranes. The basic need is for a membrane that removes water and can be used broadly.

Other polymer membranes are available. For example, polyvinyl alcohol (PVA) membranes are on the market, but they have significant temperature and chemical limitations: for example, the membranes will actually compete for the alcohol reactants. Recent introduction of a silica membrane overseas also has significant chemical limitations.⁽³⁾ For instance both PVA and silica membranes could not operate in the presence of organic acids. PVA will actually react with the acid and silica will be unstable in this acid environment. Therefore while all three of these membranes (PVA, silica, CMS) might be able to remove water from ethanol (e.g. fuel grade ethanol) only the CMS perfluoromembrane could operate in an organic acid environment for water removal and enhancing overall reaction kinetics. The development of a perfluoro membrane with exceptional water-organic separation capabilities is a truly unique, innovative and valuable product. A high water-organic separation would provide for a high extent of reaction and efficient operation, and the fact that the membrane is perfluoro in nature, means that it will have universal applicability for almost any water-organic environment. This universal applicability will be of value both to the end user as well as the fabricator. At the end user level, there should be little concern for variation in water-organic conditions, and the system can be used for a multitude of reactions. From the supplier standpoint, the applicability of one product being universally utilizable would significantly reduce overall manufacturing costs by having reduced number of applicable products in the product line. This innovation should be of significant value in the production of compounds products that have water as one of the products-of-reaction.

Also existing membranes (both organic and inorganic) are hydrophilic. Therefore at low water concentrations (e.g. 5% water in the reactor) membranes lose their water permeability. This can be seen in Figure 1⁽⁴⁾ which shows existing (PVA) pervaporation membranes have over a 10-fold loss in flux as water concentration goes from 25% to 5% (vertical lines of Figure 1). In contrast to the hydrophilic membranes, such as PVA, CMS membranes retain their high water flux at low water concentrations.

This program has addressed three barriers for membranes as outlined in the AIChE Vision 2020: 2000 Separation Roadmap.⁽⁵⁾

Figure 1. Dependence of Water Flux on Feed Concentration⁽⁴⁾

³ Sommer, S., Klinkhammer, B., Melin, T.: Integrated system design for dewatering of solvents with microporous silica membranes, Desalination 149 (2002) 15-21

⁴ Bartels, et al., Plant Evaluation of Pervaporation Process., Proceedings of Third International Conference on Evaporation Processes in the Chemical Industry., pg.486-493, 1988, Bakish Materials Corp.

⁵ Vision 2020: 1998 Separation Roadmap, New York: AIChE, Waste Reduction Technologies, October 1998

Specifically:

- ✓ Development of high temperature membranes.
- ✓ Chemically resistant properties.
- ✓ Need for low cost membrane reactor systems.

CMS Membranes: The Compact Membrane Systems (CMS) membrane has extremely high ruggedness and gas transport associated with its perfluoro nature and high free volume. Due to these unique characteristics CMS membranes are not affected by harsh environments and can achieve satisfactory levels of separations, even at high temperatures. CMS polymers are amorphous, highly transparent and their chemical perfluoro nature allows them to be stable under high temperatures and harsh conditions. At present, there are no other polymeric membranes that are used at high temperatures and under harsh conditions (e.g. 130°C with organic acid).

CMS membranes have extremely high gas permeability and are characterized by very large free volume (e.g. 33-36%): the average radii of free volume elements in them are about 5-6 Å, that is, much larger than those in other polymers ⁽⁶⁾. The result implies that permeation rates in these polymers would be high. It is also worth noting that CMS membranes exhibit several properties important for pervaporation: insolubility in most organic solvents, excellent chemical and thermal stability, and very good film forming properties. Many of the characteristics of CMS membranes have been presented in the following reference ⁽⁷⁾. Perfluoro-2,2-dimethyl-1,1,3-dioxole (PDD) copolymerized with tetrafluoroethylene (TFE) (see Figure 2) represents a new family of glassy membrane materials which should be applicable to this purpose of water-organic separation. CMS-3 and CMS-7 are PDD-TFE copolymers with different copolymer ratios; CMS-3 has 65% PDD and CMS-7 has 85% PDD.

Overall Technical Approach and Anticipated Results

Through completion of the planned research program, Compact Membrane Systems (CMS) and KSE, Inc. (KSE) developed a technology for Reactive Membrane Systems for Vinyl Ether Synthesis. The completed research provides a new building block for organic chemical synthesis; the program can produce major structural changes in the method of manufacture and the energy usage of certain large volume chemicals. The first two years of this program entailed successful research and development.

In this program, KSE is combining its expertise in catalysis and reactive separations with that of the CMS, a leader in the development of high temperature, robust membrane systems. The program combines the energy efficiency and process integration of membrane separations with new catalysts tailored specifically for membrane applications. From this successful research

⁶ Nemser, S., Yampolskii, Y., Alentiev, A., Shantarovich, V., Plate, N.: High Transport Parameters and Free Volume of perfluorodioxole copolymers, Journal of Membrane Sciences 126 (1997) 123-132

⁷ Yampolskii, Y., Polyakov, A., Starannikova, L.: Amorphous Teflons AF as organophilic pervaporation materials Transport of individual components, Journal of Membrane Sciences, 216 (2003) 241-256

program, the energy usage in chemical processing in certain major plants can be reduced by 50%, the associated carbon dioxide emissions are reduced, the process complexity and byproducts disposal requirements are reduced, and the manufacturing costs of certain large volume chemicals are dramatically reduced. Improvements of this magnitude are needed to address the structural impacts on the chemical industry described above, and would be a direct result of the part played by this research program.

Through the research reported herein, CMS and KSE have established the technical merit and feasibility of extending the field of reactive membrane applications to include vinyl ether synthesis in general and methyl vinyl ether (MVE) synthesis in particular. Reactive membrane systems utilize close coupling of the membrane and chemical reactor systems, enabling operation in fewer process units, enhancement of yield of the desired product, and/or reductions in energy consumption and capital investment. Again, these attributes precisely address the current needs of the chemical industry.

Vinyl ethers have long offered the opportunity to provide potential building blocks for organic chemical synthesis. To date, however, primarily high margin applications have been exploited for vinyl ethers, because of their processing complexity and historical high cost of manufacture. The results of the present program have demonstrated that the new reactive membrane technology can provide the cost and energy efficiencies necessary to recapture the opportunities offered by vinyl ether chemistry to the U.S. Chemical Industry.

Opportunities for Energy Efficiencies

MVE can be used as an intermediate to produce PVOH. This process is an alternative to the present commercial route of manufacture which is indirect, complex and energy inefficient. By comparing the two routes in terms of energy requirements, the potential impact of this research program can be ascertained.

As a first estimate for the comparison, methods developed for life cycle assessment (LCA) are useful. Cumulative Energy Requirement Analysis (CERA) is one aspect of LCA that quantifies the energy demand that arises from production, distribution, and use of a product.⁸ Boustead⁹ describes a methodology for performing energy assessment, including upstream energy demands and the current process energy demands. While this is one basis for energy assessments, and many methods are similar, Patel¹⁰ provides one of the few sources of consistent data.

Patel provides data for the energy analysis of chemical processes based on chemical intermediates and plastics produced in Germany.¹⁰ Patel provides an energy assessment based on two factors. The first is Net Caloric Value (NCV). NCV is a measure of the energy of combustion in a material, defined as the heat evolved when all of the combustion products are cooled only to the point where any water remains as a gas. The second is the Cumulative Process energy Requirements (CPR), which includes all the process energy involved to get from the base

⁸ Wrisberg, N. and Udo de Haes (ed), "Analytical Tools for Environmental Design and Management in a Systems Perspective", Kluwer Academic Publishers (2002).

⁹ Boustead, I., "ECO-Profiles of the European Plastics Industry: Methodology", Report for APME, Brussels, July (2003).

¹⁰ Patel, M., "Cumulative Energy Demand (CED) and Cumulative CO₂ Emissions for Products of the Organic Chemical Industry", Energy, 28, 721-740 (2003).

raw materials (usually fossil fuel sources) to the chemical being evaluated. The sum of these two contributions is the Cumulative Energy Demand (CED).

Patel provides data for the Cumulative Energy Demand (CED) and Cumulative Process energy Requirements (CPR) of many chemical intermediates. The CED is the sum of the CPR and the Net Caloric Value of the material. The total energy requirements for producing PVOH by both routes has been estimated using the Patel methodology, based on the stoichiometry, the heats of reaction, the estimated energy required for separations, and the CPR values for the raw materials.

KSE has estimated the process separations energy from extensive Aspen simulations of the expected separations for the conventional Vinyl Acetate Monomer (VAM) route, and from the reactive membrane design for the MVE route developed in the present program. For the VAM route, a patent¹¹ and separation energies reported in an article by DuPont¹² were also used. The energy use for the final polymerization step of the two alternative production methods is not included, because both routes have similar energy requirements for this polymerization step.

Table 2 provides a comparison of these energy estimates, showing the energy savings from the proposed program. It is noteworthy that the proposed reactive membrane technology can literally cut energy usage for PVOH production in half. Considering that incremental improvements in energy consumption often achieve a few percentage points reduction in energy usage, the large energy savings offered by the Phase II technology are remarkable.

Table 2
Energy Savings from Proposed Reactive Membrane Program
When applied to Polyvinyl Alcohol Manufacture
GJ/MT Polyvinyl Alcohol

	Energy Balance
Conventional Energy Consumption ^a	106 GJ/MT
Forecast Reactive Membrane Technology ^b	52 GJ/MT
Energy Savings, U.S. Industry	8 Trillion BTU/yr.

^a**VAM Route:** Conventional Vinyl Acetate Monomer Sequence to Polyvinyl Alcohol

^b**KSE MVE Route:** KSE MVE Technology to Polyvinyl Alcohol

From Table 2, the MVE route requires only one-half the energy of the VAM route to manufacture PVOH, saving 54 GJ/MT of PVOH. For the total US production of PVOH of 375 million lbs/yr, that would be a savings of 8 trillion BTU/yr. Furthermore, there are significant savings in all categories of raw materials, heats of reaction, and separations.

Increasingly, energy pricing is a global phenomenon. A reduction in energy usage anywhere in the world will result in a reduction in imported oil price pressures in the U.S. On this basis, the total worldwide PVOH production is 1.3 billion annual pounds. The potential opportunity offered by the reactive membrane technology would thus become 30 trillion BTU/yr.

Furthermore, this energy savings represents application of the reactive membrane technology to only one product, PVOH. It is the direct result of eliminating virtually one-half of the energy consumption of the entire process. The U.S. chemical industry has been working on energy conservation for decades, and, by now, a few percentage points of savings is often a major

¹¹ Karim, K. et al., "Method for producing vinyl acetate monomer from Ethane or Ethylene Oxidation", U.S. Patent 6,605,739, August 12 (2003).

¹² Luyben, M.L. and B.D. Tyreus, "An Industrial Design/Control Study for the Vinyl Acetate Monomer Process", Computers, Chem. Engng., Vol 22, No. 7-8, pp. 867-874, 1998.

accomplishment. By a radical change in the manufacturing technology, the reactive membrane technology has the potential to cut the energy consumption of the entire PVOH process in half. Ultimate energy savings to the chemical industry could be many-fold greater, with application of vinyl ethers to the other existing markets beyond PVOH and the additional new markets created by the low cost vinyl ethers.

The objective of the third year was a successful demonstration of the technology involving commercial companies. As a result of this effort, CMS has identified critical technology requiring more research. With new funding, CMS is poised to demonstrate and commercialize a novel reactive technology to produce vinyl ethers that avoids the shortcomings of the existing manufacturing methods.

3. Results and Accomplishments

Task 1: Fabricate Membrane Reactor System with CMS-3 Sheet Membrane

Completion of this task included fabrication of prototype membrane reactors based on perfluoro membranes on perfluoro supports in perfluoro shells with perfluoro potting material. CMS presently has multiple membrane reactor modules. These reactors allowed us to accelerate evaluation during this and subsequent phases of the program. Membrane modules have approximately ten square feet and are projected to have upper use temperatures well in excess of 150°C.

Working with our collaborators we have identified catalyst systems to enhance the synthesis at low temperature (e.g. 150°C versus 200°C).

Early Membrane Reactor Module Work -- Membrane reactor were installed in the reaction loop. Preliminary testing of key reaction components and associated support evaluation has been completed. In parallel with our key high temperature evaluations (e.g. 150°C) we demonstrated that the CMS membrane reactor provided enhanced synthesis by increasing reaction rates 6-fold and also provided for overall higher yield. While these demonstrations were done in parallel and not on our high temperature reactor, they clearly demonstrated the potential of the CMS membrane reactor to enhance synthesis.

With prototype membrane reactors in place, we also demonstrated feasibility of increasing operating temperatures with an approximately 20-fold improvement in reactivity per unit dollar of membrane module costs. However, problems with the porous supports developed at this stage, and needed to be addressed in the next section of this report.

Enhanced CMS Composite Membranes: Porous Support Work -- While our CMS membrane being perfluoro in nature has superb chemical and thermal resistance, the porous support planned for this program became the chemical and thermal limitation of the overall system. The existing commercial polysulfone support did not appear to have sufficient chemical resistance for large scale operation. Therefore we significantly expanded the evaluation of porous supports. Specifically, we are evaluating new porous supports, designated as “A”, “B”, and “C”. A, B, and C, shown in Table 3, have superb chemical resistance.

We had initially hoped to use our first generation membranes based on the CMS microporous polysulfone supports. These are commercial products. They are presently used to remove gases from transformer oil and they are easily available for evaluation as well as subsequent commercialization. Initial tests with these materials proved that the system was unstable in the MVE application environment. Specifically, there was delamination between the CMS

membrane and the microporous polysulfone support. Fortunately, we quickly developed back-ups as described below.

In parallel efforts with company ‘A’ as well as company ‘B’ we looked at microporous A and B porous hollow fiber (HF) supports. Table 3 summarizes the properties of these porous supports from a chemical standpoint as well as an initial CMS composite membrane evaluation separation standpoint (Figure 3C). The composites of CMS membrane on the A and B porous supports were fabricated in a similar manner to the procedures that we used for fabricating the CMS membrane on polysulfone. Table 3 shows that A and B have far superior chemical resistance.

Therefore we demonstrated the fabrication of new chemically resistant CMS composite membranes. We have both A systems from ‘A’ and B systems from ‘B’. The majority of work was done with the A materials. The A is commercial today while the B is at a more developmental stage. Also, please note ‘A’ committed \$1,000,000 to ongoing development of the A hollow fiber in support of CMS. As an indication of resistance, the A can operate up to approximately 130°C and the B can operate over 200°C.

Table 3A
New Porous Supports – Hollow Fiber

Material	Comm. Status	Upper Use Temp.	Chemical Limitations				Mem. Thickness (microns)
			Overall	Alcohols	Ketones	Acids	
Polysulfone	Comm.	160°C	Fair	Very Good	Poor	Poor	0.3
A	Comm.	160°C	V.Good	Exc.	Poor	Good	0.3
B	Dev.	250°C	Exc.	Exc.	Exc.	Good	0.3
C	Dev.	250°C	Exc.	Exc.	Exc.	Exc.	3.0

Table 3B. Chemical Resistance of CMS Porous Supports

Polymers	C	A	B	Polysulfone/ Polyethersulfone
Chemicals				
Acids				
Acetic	R	R	R	R/N
Nitric	R	R	N	L/N
Sulfuric	R	R	N	R/N
Gases				
Carbon Dioxide	R	R	R	R
Methane	R	R	R	R
Ozone	R	R	R	N
Solvents				
Acetone	R	N	R	N
Isopropyl Alcohol	R	R	R	N
Hydrocarbons				
Iso octane	R	R	R	R/L
Xylene	R	R	R	L

R = Recommended; L = Limited Recommendation; N = Not Recommended

Table 3C
CMS-3 Membrane Performance for Various Supports

Support	Membrane Thickness (microns)	Selectivity		
		O ₂ / N ₂	He / N ₂	N ₂ / Propane
Polysulfone	1.0 – 2.0	2.5	10.5	13
A	1.0 – 2.0	2.5	10.7	13 – 14
B	1.5 – 2.5	2.6	---	13.8

Table 3 summarizes the initial findings on these materials (e.g., A and B) in cases where a mini-module is used to evaluate the porous support.

Porous support B has excellent chemical and thermal resistance. Therefore since Table 3 shows excellent performance with our B porous support, additional work was focused on the CMS-B composite system. Porous support B has upper use temperature in excess of 200 °C and superb chemical resistance (with the exception of exposure to strong acids).

Using our existing commercial infrastructure and the laboratory results from above on CMS – B porous support systems, we fabricated larger diameter CMS – B composite structures. First we fabricated 2” diameter membrane modules containing approximately 7,000 cm² of surface area (the earlier laboratory results were for less than 100 cm² of surface area). Table 4 summarizes the results for our initial testing of this 2” diameter module and compares results to the standard CMS-microporous polysulfone control. Table 4 shows that our initial attempt with CMS-B systems was successful and produced a product that should pass commercial performance specifications.

Table 4. CMS-B Testing vs. Specification 2” Diameter Module

	CMS – B	CMS – Polysulfone Specifications
Nitrogen Flux (GPU)	156	>100
O ₂ /N ₂ selectivity	2.4	>2.3
Oil Leakage (a)	0	<8 ml
GPU = CM ³ / CM ² – sec-emltg x 10 ⁻⁶		
(a) 4 hr Test, 45 psig, 60 ⁰ c		

Given success with the 2” diameter units in Table 4, we next evaluated the 4” diameter device which contains up to 50,000 sq. cm of material and is used commercially for venting air from underground gasoline stations in California. Table 5 summarizes the results for testing in the air venting/CARB application and again compares the CMS membrane – B porous support to the standard CMS membrane –polysulfone porous support product. Table 5 also compares favorably and indicates that we have successfully made 4” diameter modules with performance with CMS – B comparable to CMS-polysulfone. This shows that we have expanded membrane module capability beyond a few fibers to full size commercial devices.

Table 5
CMS-B Tests vs. Specification
4" Diameter Module

	CMS – B (a)	CMS – Polysulfone Specifications
Nitrogen Flow (SCFM)	0.19	>0.18
N ₂ Propane selectivity	12.3	>11
(a) Average of Two Modules		

This was a success far in excess of the program's original expectations. Within the limited time frame of this program (e.g., less than two years) we have gone from no evaluation of the CMS-B system to taking commercial orders.

CMS has become commercial with membrane modules based on the CMS-3 membranes on polysulfone and polyethersulfone hollow-fiber porous supports. In addition to polysulfone and polyethersulfone porous support, Asahi Chemical has provided CMS with attractive new microporous hollow fiber supports based on hydrophobic PVDF (polyvinylidene fluoride). Table 6 shows initial gas testing of these PVDF hollow fibers and compares them to polysulfone and polypropylene hollow fibers. These PVDF hollow fibers appear to have very high gas transport and may make ideal supports for CMS membranes. Table 6 shows that PVDF has both the high gas flux approaching polysulfone but the bubble point and He, O₂, N₂ flux suggest Knudsen flow consistent with small pore size on surface. This combination provided an excellent arsenal of raw materials for the evaluations that demonstrate feasibility of water byproduct removal from reversible reactions. We have the commercial polysulfone and polyethersulfone porous supports with the CMS-3 membrane and the PVDF porous hollow fiber in-house from Asahi Chemical. Therefore we have fabricated PVDF porous hollow fibers into composite membranes. Then, using our existing coating and winding line we fabricated the coated fibers into actual modules similar to the commercial polysulfone and polyethersulfone based modules.

CMS standard wound modules have excellent mass transfer capabilities for removing low concentrations of dissolved gases or liquids from the bulk liquid. The wound fibers provide for enhanced mixing. Flow patterns through wound hollow fiber configurations lead to higher mixing levels and minimize the chances of concentration polarization. This has been extremely important in those applications where there are only modest levels of the component that is desired to be removed. In this particular case that component is the water byproduct from the reaction under consideration. While there is a level of concern for mass transfer limitations in this liquid separation, given the success we have had with the commercial design used for modules to date we will focus initially on this existing wound design that has been excellent performance for removing low-concentration gases from transformer oil. While our focus has been on the porous supports above, we also have other potential porous supports. Specifically we have microporous expanded polytetrafluoroethylene (ePTFE) hollow fibers and PEEK (polyether ether ketone) hollow fibers.

Table 6A
Permeability of PVDF versus Other Fibers

Fiber Species	Gas Species	Permeance (K-GPU)
Polysulfone 1 (MEDAL)	Nitrogen	39
Polysulfone 2 (MEDAL)	Nitrogen	91
PVDF (<i>prelim. Data</i>)	Nitrogen	50
Polypropylene (Celgard X30)	Nitrogen	11
Polypropylene (Celgard X50)	Nitrogen	10

$$\text{GPU} = 10^{-6} \text{ cm}^3 / \text{cm}^2\text{-sec-cmHg}$$

Table 6B

Gas Permeance (K-GPU)		
N ₂	O ₂	He
180	160	300
Selectivity		
O ₂ / N ₂	He / N ₂	He / O ₂
0.94	1.79	1.90

Table 6C

PVDF Bubble Point
Above 20 Psig (as measured in IPA)

Despite initial promising results, our work with PVDF porous substrates was discontinued. PVDF does not wet, during the application of the CMS membrane material, as reproducibly as PEEK porous substrates. It also tends to swell and delaminate when exposed to chemicals like ethanol and acetic acid.

We have identified PEEK as a suitable porous support for the CMS membrane. PEEK has an excellent chemical and thermal resistance and is ideal for use with aggressive chemicals at high temperature. We have found a supplier of PEEK microporous hollow fibers and have obtained sufficient amounts of fiber to build 7 ft² and larger modules. Various CMS-3/PEEK membrane modules were manufactured and were available for testing.

Chemical Resistance of Materials of Construction for the Membrane Modules

We encountered a significant technical problem with supports and epoxies that were not sufficiently resistant to the chemicals involved in this program. The CMS components used in this system in combination with the B porous support can operate at the systems level up to around 140 C. By switching from the CMS-3 membrane to the CMS-7 membrane the CMS-7/porous support B system should be able to operate up to 200 C (and possibly above). Parallel to these higher temperatures the system should be able to handle more aggressive solvents (e.g., ketones). While the CMS membranes and the B porous support can handle these high temperatures the epoxies used in these systems were designed for low temperature operations (e.g., air venting and degassing transformer oil) with maximum operational temperatures of around 100 C. Therefore in order to fully capture the high temperature and chemical resistance of the system it was necessary to reformulate and/or modify the process so the potting systems will not cause systems limitations. This reformulation and/or process modification was given a high priority.

The reaction constituents are extremely aggressive to many polymeric materials, causing swelling, deterioration, and failure of the materials. There are three components to the membrane module, (1) the membrane itself, (2) the membrane support, and (3) the potting compound used to bind the membrane hollow fibers into the module. From a review of the trade

literature, the first two of these materials are judged to be compatible with the chemical constituents described above, and at the reaction conditions. Chemical compatibility tests have therefore focused on the potting compounds. The exact compositions of these three materials were maintained proprietary to CMS.

Chemical resistance evaluations measured the weight gain of samples of the potting compound when immersed in the various chemical components. Such tests are commonly used in the polymer industry, and KSE has had decades of experience with the use of such accelerated tests to judge the long term performance of polymers. Although simple, these tests provide substantial insight into the chemical resistance characteristics of polymers.

The evaluations have focused on the first stage membrane for the intermediate DMA purification¹³. Previous results had shown that the standard membrane module potting compounds showed significant weight gain, up to as much as 3% over a 1000-hour immersion period, in a liquid mixture simulating the equilibrium composition for Reaction (2)¹³. Although not necessarily predictive of failure, such a level of swelling represented a concern. Efforts were undertaken to identify and evaluate potting compounds with improved resistance to the chemical environment of the first stage membrane module.

Improved potting compounds were evaluated using the same Reaction (2) equilibrium mixture. Results for liquid-phase exposures at a typical reaction temperature of 20°C are summarized in Figure 3 below.

Figure 3
Weight Gain of Potting Compound Samples Immersed in Liquid Components
at 20°C (Reflects Swelling of Material)

¹³ Acetaldehyde + Methanol $\leftrightarrow$ MVE + Water (1),
consists of the two reactions
Acetaldehyde + 2 Methanol $\leftrightarrow$ 1, 1 Dimethoxyethane (DMA) + H₂O (2)
DMA $\leftrightarrow$ MVE + Methanol (3)

After an exposure time of approximately 650 hours, swelling for the samples of the improved potting compound was approximately 0.34%, a factor-of-8 lower than the standard potting compound evaluated previously. This represents a substantial improvement in chemical resistance, and provides a level of performance more consistent with long-term operability in the liquid-phase chemical environment for a first stage membrane.

Samples of the improved potting compound were also exposed to the stoichiometric mixture of methanol and MVE at 125°C simulating the environment of the second stage membrane. The standard potting compound had experienced a weight gain of about 4% after only 23 hours in this vapor exposure. Weight gain for the improved potting compound in the same exposure environment and time frame was much less than 1%, again representing a substantial improvement. With extended exposure, the improved potting compound did experience weight gain exceeding 4%, indicating that further improvement should be considered. It should be recognized, however, that the accelerated performance test conditions used here are more severe than seen in commercial applications.

CMS-3/PEEK Membrane Modules: Using the potting compound information from above (Figure 3) we fabricated pilot test modules using this preferred potting system. Table 7 shows the results of this fabrication. The four membrane modules in Table 7 were made using CMS-3 amorphous perfluoropolymer, PEEK (polyether ether ketone) hollow fibers, and the newly developed potting material. Table 7 shows O₂/N₂ and He/N₂ selectivity comparable to thick CMS film: these results suggest minimal defects in the four modules. We chose from these modules for testing the MVE synthesis at KSE.

Table 7
High Temperature Modules

No.	Module No.	<i>2HT Cartridges</i>					
		Area (ft ²)	α (He/N ₂)	α (O ₂ /N ₂)	P/t He EU	P/t O ₂ EU	P/t N ₂ EU
1	2HT72	9.4	14.6	2.64	14.4	3.85	1.46
2	2HT73	9.4	13.1	2.64	13.1	3.42	1.29
3	2HT74	9.5	10.5	2.72	12.3	3.21	1.18
4	2HT75	9.5	9.9	2.65	11/7	3.13	1.18

P/t = ncft/ft²-day-psi

CMS Thick Film Selectivity (α): $\alpha_{O_2/N_2} = 2.68$; $\alpha_{He/N_2} = 11.5$

The problems associated with the porous support and epoxy potting were identified, and we have accomplished the following results in our laboratory:

(A) Developed a new epoxy and using epoxy coupons have evaluated the epoxy's chemical resistance to chemicals of interest both at room temperature and at high temperature. Laboratory evaluation has shown that this material is far superior to our original epoxy formulation.

(B) We have shifted from the original hollow fiber PVDF porous support for our CMS amorphous perfluoromembrane to a new porous support, PEEK, which has a much greater

chemical resistance than PVDF. This improvement in chemical resistance is based on direct laboratory tests. CMS has prepared CMS composite hollow fiber membranes on PEEK hollow-fiber support and tested them at 130°C with ethanol, and demonstrated that the CMS membranes on the new porous supports are able to maintain their performance over extended tests.

Combining the results from (A) and (B) we prepared 10 ft² pilot scale membrane modules for evaluation of water removal from mixtures of water, acetaldehyde, ethanol, DEA, and EVE. We manufactured two CMS-3/PEEK membrane modules.

A 10 ft² membrane cartridge, labeled 2PG93, consisting of PEEK fibers coated with CMS-3 was potted with a new epoxy, which is temperature resistant and chemically resistant. As described below, we obtained optimum membrane performance from this cartridge.

Table 8 summarizes the results for various CMS-3 membranes coated on various supports, which include the scaled-up module 2PG93 made with PEEK hollow fibers. Notice that the comparison involves different substrates and membrane areas. The flat membranes were made by two passes of spray coating. The hollow fiber was dip coated on the outside of the hollow fiber.

Table 8. Scale-up of CMS-3 membrane from flat sheet to hollow fiber.

Membrane Type	Substrate	Area (ft ²)	Test Temp. (°C)	Water Permeance (GPU)	H ₂ O/EtOH Selectivity
Flat Sheet	PAN	0.1	120	687	18
Flat Sheet	ePTFE	0.5	105	660	18
Flat Sheet	PAN	1.5	120	1100	21
Hollow Fiber	PEEK	10	120	1500	20

The selectivity obtained with the 10 ft² module is at least as good as that obtained with small flat sheet modules. The scaled-up module's flux is larger than the flux obtained with the small flat-sheet modules, which is attributed to the thinner coating achieved in the hollow-fibers module. Therefore, we have successfully scaled up the membrane module from 0.5 ft² flat sheet membrane to 10 ft² hollow fiber module.

Task 2: Enhanced Synthesis of MVE (methyl vinyl ether) or EVE (ethyl vinyl ether) (KSE)

Vinyl ethers are widely used in chemical industry, as monomers for important polymerization reactions, adhesives, pressure sensitive tapes, water sensitized adhesives, polishes, lube oil additives, and the like. In addition to these uses, methyl vinyl ether (MVE) is also used as a raw material for biocide manufacture, such as glutaraldehyde, which will be of growing importance to protect against bioterrorism. The total annual market exceeds several hundred million pounds. However, manufacturing methods for vinyl ethers remain inefficient, using toxic solvents, producing excessive byproducts, and requiring handling of hazardous materials. Current commercial methods often employ variations of the old Reppe chemistry, such as the energy intensive acetylene route based on World War II technology. This research program proposes to complete the research necessary to commercialize a novel reactive membrane technology to produce vinyl ethers, avoiding the shortcomings of existing manufacturing methods.

To avoid the Reppe chemistry, two inexpensive reactants are used to produce MVE: acetaldehyde and methanol. The overall reaction is shown in Equation (1)

In fact, this reaction proceeds in two stages. In the first stage, shown in Equation (2), the acetaldehyde and methanol react to form an intermediate, dimethoxyethane, or DMA¹⁴. In a second stage, this DMA is further reacted to form the desired product MVE, in Equation (3). A byproduct in Equation (3) is methanol, which is recycled to the first stage.

The reaction and separation system using conventional technology is inefficient and ineffective. The reaction of Equation (2) is limited to about 50% to 70% conversion, due to equilibrium limitations. Also, the DMA product and the unconverted methanol have almost identical boiling points, within one degree of each other. Furthermore, there are azeotropes of DMA and water, and of DMA and methanol, which complicate purification by traditional fractionation methods.

The second stage reaction, Equation (3), is an endothermic reaction. In order to achieve high equilibrium conversions in an endothermic reaction, high temperatures are required. This, along with the comparatively inactive commercial catalysts, requires the second stage reaction to be conducted at about 250°C to 300°C. In turn, the high temperature and the current commercial catalysts produce poor reaction selectivity associated with Equation (3), principally with a variety of ethers formed.

The conventional MVE synthesis technology thus requires multiple reactors, with over six separation and purification distillation columns, and with the attendant unconverted reactant recycle and byproduct disposal. Because of all these practical limitations, vinyl ethers are generally difficult and costly to produce, and MVE is no exception. The process shown by equations (2) and (3) is currently used by Daicel in Japan to produce MVE from acetaldehyde and methanol. Dow Chemical Company uses this approach in the U.S., in order to produce MVE for use in glutaraldehyde manufacture. The conventional MVE plant is quite complex, as shown in Figure 4. This conventional technology employs a stirred tank reactor for Reaction (2), using a sulfuric acid catalyst with about 50% conversion as limited by equilibrium. The product is sent to a train of distillation columns to separate unconverted methanol and acetaldehyde, but the degree of separation is severely limited by the azeotropes referenced above. Extensive recycle is required. When purification is finally achieved, the DMA/methanol azeotrope is vaporized and reacted at temperatures near 300°C over a basic catalyst. Again, conversion is limited by equilibrium, and substantial loss of DMA to byproducts is encountered. In addition to the columns shown, four additional distillation columns are needed to separate unconverted reactant, azeotropes, and byproducts. The major objective of the present program has been to reduce this complex conventional plant layout into a simple plant containing just two reactive membrane systems. Schematic 1 shows the process flow sheet for the MVE (or EVE) product using the membrane reactor technology.

¹⁴ The intermediate compound 1,1-dimethoxyethane is also known as dimethylacetal, or DMA.

Figure 4. Conventional Technology for MVE Synthesis: Complex and Costly

The membrane reactor system to produce MVE still utilizes catalyzed reactions between acetaldehyde and methanol. Both reactants are inexpensive and widely available. The intermediate compound is DMA. Although DMA has other valuable commercial uses, it was considered only as a reaction intermediate for MVE in these investigations. Also, additional side reactions not shown in Reactions (2) and (3) can occur under specific experimental conditions, which are quite important to membrane reactor assessments. For example, acetaldehyde can itself undergo a number of side reactions with acidic catalysts, unless its composition is maintained below that of methanol when in contact with the catalyst.

Schematic 1. Process Flow for Membrane Reactor System

Reaction (2) is exothermic and reversible, and can proceed with an acidic catalyst at about 60°C, but with only about 50% maximum conversion as constrained by equilibrium. Membrane dewatering will obviously reduce the limitations of this equilibrium constraint. Operation at lower temperatures will improve the equilibrium conversion somewhat, but at the expense of lower reaction rates.

New catalysts for Reaction (2) have been developed by KSE Inc. These catalysts are highly active, being capable of achieving the equilibrium conversion in a reactor residence time of seconds, in the liquid phase. An example of the performance of the first stage catalyst is shown

in Figure 5. These catalysts are sufficiently active and selective that operation at low methanol feed ratio is possible, to be followed by separation of products in a membrane unit. As will be noted later, the membrane unit is able to remove both water and methanol from the reactor effluent. Hence, not only is the reaction of Equation (2) able to be driven to the right, but also the methanol is removed, thereby circumventing the problems of the methanol-DMA azeotrope and the close boiling points of methanol and DMA. These factors greatly reduce the energy consumption of the process.

Figure 5
Acetaldehyde Conversion to DMA
Catalyst No. CATH251W

The reaction of Equation (3) is endothermic and reversible. It can proceed with a catalyst at about 200°C, but with only about 50% maximum conversion as limited by equilibrium. Higher conversion requires temperatures approaching 300°C. KSE has discovered second stage catalysts which can be operated at about 125°C. The selectivity of the catalyst system is also excellent, as shown in Figures 6 and 7. As noted, the improved selectivity greatly enhances the energy consumption required for purification of products.

Of course, the reaction equilibrium is unchanged for these highly active second stage catalysts, which limits the overall conversion achievable. As will be noted below, the membrane system is able to operate at 125°C, and will pass both MVE and methanol, while retaining DMA. Therefore, the membrane system will remove the products, which circumvents the limitation of the equilibrium on overall conversion of DMA to MVE.

Figure 6
Product Yield Comparison
KSE Catalyst at 125°C versus Commercial Catalyst
 Dimethyl Acetal $\leftrightarrow$ MVE + Methanol

Figure 7
Comparison of MVE Selectivity for
KSE Catalyst at 125°C and Commercial Catalyst
 DMA $\leftrightarrow$ MVE + Methanol

Task 3: Optimize Operation of Perfluoro Membrane Reactor System (CMS, KSE)

Early in the program tests were performed with a CMS-7 membrane system in a pervaporation mode, to examine its ability to retain DMA, and to permeate one or more of the following first stage components (see Equation 2 for the components). As shown in Figures 8 and 9, the CMS-7 membrane structure is too open for this application, in that it passes both DMA and methanol. Note, in particular, that the concentration of both components in the permeate are similar, indicating poor membrane selectivity.

Figure 8

Figure 9

In Figure 10, a similar result of poor pervaporation selectivity is shown for the CMS-7 membrane between methanol and water. In Figure 10, the permeation rate through the membrane is shown, as a function of the composition of methanol in water. Here, as the methanol

concentration is increased, the overall permeation rate is seen to also increase. This indicates that the membrane is not selectively passing water and retaining methanol. Instead, both methanol and water are passing the membrane. This is not surprising, as the tests reported in Figures 8 and 9 indicated that DMA, methanol and water are all passed through the membrane, at similar rates.

Figure 10

It is obvious that the CMS-7 membrane structure is too open for this application, and the future work would be with CMS-3 membrane structure.

Synthesis of Ethyl Vinyl Ether

Ethyl vinyl ether (EVE) is a close analog to MVE, and is utilized as a polymerization monomer in the production of EVE polymers and copolymers. EVE polymers and copolymers are used in a wide variety of elastomer and adhesive application, especially for medical adhesives, and other water-soluble adhesives^{15,16,17}. There is a substantial commercial market for EVE monomer on a global basis^{18,19}.

Ethyl vinyl ether can be synthesized from acetaldehyde and ethanol, with diethyl acetal (DEA) as in intermediate, in a manner directly analogous to the synthesis of MVE from acetaldehyde and methanol, with dimethyl acetal (DMA) as the intermediate. Reaction conditions and reaction equilibria have been found to be very similar for the synthesis of the DMA and DEA

¹⁵ Pawelchak, J.M., et al, "Adhesive Compositions", US Patent 4,393,080, July 12, 1983

¹⁶ Rawlings, D.A., et al, "Surgical Dressing", US Patent 4,657,006, April 14, 1987

¹⁷ Martin, M., Adhesives Research, private communication, June 20, 2008

¹⁸ "Vinyl Monomers and Vinyl Compounds", BASF;

<http://www.basf.de/en/intermed/products/vinylmonomers/vinylether.htm>

¹⁹ Li, C., BASF, Private Communication, December 19, 2008

intermediates. The synthesis of EVE from DEA has also been found to be remarkably similar to synthesis of MVE from DMA.

The boiling points of DEA (102°C) and water (100°C) are extremely close, making separation by distillation exceedingly difficult. Membrane separation offers a highly attractive alternative for the separation of DEA and water. In addition, the overall components for the DEA system are very similar to the separation of water and ethanol, an application for which membrane separation has been very successful. Because of the near-term commercial applications, KSE is utilizing DEA/EVE synthesis in the membrane evaluation program, and as a prototype system for DMA/MVE synthesis.

Ethyl Vinyl Ether (EVE) synthesis is conducted in two steps. In the first step, acetaldehyde and ethanol are converted to Diethyl Acetal (DEA) and water. The second step converts DEA to EVE and ethanol. In the vinyl ether synthesis, the first membrane unit is to separate and purify DEA, in order to drive the equilibrium-limited DEA formation reaction. This reaction can operate between 0° C and 100° C, with higher temperatures causing a lower equilibrium conversion. Stoichiometric coefficients have been omitted in the equation below.

Separation by distillation is difficult and highly energy intensive. The boiling points of DEA (102°C) and water (100°C) are extremely close, making separation by distillation exceedingly difficult. The membrane can effectively drive the reaction to completion by removing water, at considerable energy savings.

The purified DEA is then fed to a second stage reactor to convert DEA to the desired product, EVE, as shown below. Again, stoichiometric coefficients have been omitted from the equation. Although usually operated at 300°C with conventional catalysts, this reaction can be operated between about 100° C and 125°C. Compared to the conventional catalysts that operate near 300°C, the KSE catalyst is dramatically more active than conventional catalysts, permitting lower temperature operation compatible with the CMS membrane system. At low temperatures, the equilibrium conversion is lower, needing the membrane unit to drive the reaction to completion.

The reaction product contains all three components, and separation is limited by several distillation azeotropes between DEA, water, and ethanol. At low temperatures, the reaction equilibrium limit is such that DEA always remains in the product mixture.

The second membrane unit removes ethanol, residual acetaldehyde, and other impurities from the unconverted DEA reactant, allowing efficient recycle of DEA to the feed of the second reactor. EVE is readily separated from ethanol, which is recycled to the first stage reactor. CMS provided CMS-3 modules, with different permeabilities, as needed.

Separation Efficiency of DEA

The results of pilot tests showed that DEA is preferentially concentrated in the retentate. All other components except DEA were concentrated in the permeate. The separation factor in Step 1 (Reaction 4) was about 6 and the separation factor in Step 2 (Reaction 5) was about 5. While these separation factors were high they were not as high as we expected. Therefore it becomes desirable to increase the selectivity of the CMS composite membrane in actual use. This increase in selectivity can come from either a modification of the base polymer (e.g., changing of the

PDD-TFE ratio) or can be obtained from appropriate post treatment procedures. Enhanced post-treatment should become obvious from the discussion below and the subsequent testing to date.

Table 9 shows that when we dry the membrane at higher temperature we actually reduce the transport of organics through the membrane. Mechanistically based on our understanding from other evaluations at CMS, this reduction in transport by higher heat treating relates to removal of any residual casting perfluorinated solvent from the CMS membrane. With the removal of that solvent there is less likelihood of exchange of that perfluorinated solvent with the feed organics. The exchange of feed organics with residual casting perfluorinated solvent leads to higher transport of the organic feed (which is undesirable through the CMS membrane). Based on our previous experience with polysulfone support, we have been limited to heat treatment temperatures of up to 120° C. Higher heat treatment temperatures lead to a collapse of the microporous polysulfone structure.

The challenge was to heat treat the fibers at higher temperature and preferentially above the T_g of the CMS membrane. The T_g of the CMS-3 polymer is 160°C. By operation above the T_g we could increase the mobility of the CMS membrane and therefore remove most or all of the

Table 9. Effect of membrane processing temperature on solvent permeance	
Film Drying Temperature	Hexane Permeance (lit/m²-hr-bar)
60 °C	1.6
120 °C	0.54

residual solvent from the membrane and in so doing as mentioned before reduce the transport of organic feed through the membrane. Fortunately part of this program associated with the high temperature operation was a development of the microporous PEEK (polyether ether ketone) microporous hollow fibers. These PEEK microporous hollow fibers can be operated

up to approximately 240° C. Therefore we have the opportunity to heat treat the CMS membrane on PEEK microporous support at much higher temperature and actually keep them above the T_g.

In an initial experiment we chose not to fully constrain the hollow fibers prior to the heat treatment to allow for the expected shrinkage of the fibers. Upon exposing to 170° C the PEEK fibers shrunk approximately 25%. If the fibers were constrained prior to heat treating this level of shrinkage would probably create defects in the membrane and reduce its separation efficiency. Therefore in our first test we took approximately seven or eight CMS freestanding coated PEEK hollow fibers and potted only one end with a high temperature epoxy. We then exposed these fibers to 170° C in a nitrogen atmosphere. We first observed the 25% shrinkage and then after the heat treating step we potted the other end of the fibers and measured their gas separation characteristics. The gas separation characteristics were slightly low. For instance the oxygen-nitrogen selectivity instead of being 2.4 to 2.5 was only 2.3 and the helium-nitrogen selectivity instead of being 10-12 had a selectivity of 9. This is probably due to the heat treatment process associated with the one end of the device that has been potted. This hypothesis is supported by the subsequent test described below.

In a second test we heat treated a set of fibers at 170°C in a nitrogen atmosphere. In this test the fibers were totally unrestricted. We also heat treated ten fibers in an air environment. The results of the heat treatment are shown quantitatively in Table 10 below. Table 10 shows that after we heat treated the fibers and fabricated them into mini-modules their oxygen-nitrogen and helium-nitrogen separations were comparable to the neat CMS membrane. This strongly supports that even with the significant shrinkage of 25% we have not damaged the membranes when they are unconstrained. Throughout this work we noticed there was no fiber-to-fiber sticking. There was a

potential concern that above the T_g the dense CMS membranes could soften and stick together. Based on the results in Table 10 and earlier work on low temperature heat treatment, we believe we have taken significantly more residual solvent out of the membrane and that when these fibers are placed in the membrane module systems for actual high temperature separations. The performances are expected to be better than earlier results.

Table 10. Gas permeation through heat treated modules.

Module	Gas	Permeate flowrate ml/min		Selectivity gas/N ₂
CB-HT-2	N ₂	5.88		
CB-HT-2	O ₂	14.7	O ₂ -N ₂	2.50
CB-HT-2	He	63.3	He-N ₂	10.77
CB-HT-3	N ₂	5.44		
CB-HT-3	O ₂	13.55	O ₂ -N ₂	2.49
CB-HT-3	H ₂	59.0	He-N ₂	10.85
CB-HT-4	N ₂	5.80		
CB-HT-4	O ₂	14.3	O ₂ -N ₂	2.47
CB-HT-4	He	61.75	He-N ₂	10.65
CB-HT-5	N ₂	5.75		
CB-HT-5	O ₂	14.3	O ₂ -N ₂	2.49
CB-HT-5	He	61.5	He-N ₂	10.70

CB-HT-2,3&4
CB-HT-5

170°C in Nitrogen for 48 hours.
170°C in Air for 48 hours.

We have taken significantly more residual solvent out of the membrane and that when these fibers are placed in the membrane module systems for actual high temperature separations the performances will be even better than we previously reported.

First Stage Separation Criteria -- Separation criteria for the first stage membrane have now been defined based on the observed effects of simulated compositions leaving the first membrane unit on the selectivity performance of the second stage reactor to produce EVE from DEA via the following reaction:

Separation criteria for this first membrane module are as follows:

- The first stage membrane has a target of less than 0.1% water by weight in the DEA-rich stream leaving the first stage membrane. DEA purchased for EVE synthesis selectivity testing, which provides the basis for establishing these criteria, contained 0.06% water
- The first stage membrane system has a target of less than 25% ethanol in the DEA-rich stream leaving the first stage membrane.
- The first stage membrane has a target of less than 1% acetaldehyde by weight in the DEA-rich stream leaving the first stage membrane.

Task 4 Long Term Testing

In the KSE program, the CMS-3 membrane has been operated for 70 hours of cumulative testing, with additional periods exposed to the various possible contaminants during heating up and cooling down.

Tests were run with module 2HT72 consisting of CMS-3 coated on PEEK hollow fibers and a membrane area of 10 ft². This experimental work was done at KSE Inc. over the course of about one month with daily start-ups and shutdowns. The tests were done at 110°C with feeds consisting of (A) acetaldehyde, ethanol, DEA (diethyl acetal), and water and (B) acetaldehyde, ethanol, DEA, and EVE (ethyl vinyl ether). The tests show that the membrane removes water selectively as expected and desired so the reaction conversion is shifted to the right. At the end of the month-long test the module was dried and tested with various gases to check the extent to which the module single gas permeances varied before and after the exposure to high temperature and aggressive chemicals. Table 11 shows the gas testing results.

Table 11. Gas test results on Module 2HT72 before and after exposure to high temperature and harsh chemicals.

Time	N ₂ (GPU)	O ₂ (GPU)	He (GPU)	O ₂ /N ₂	He/N ₂
Before	101	268	1094	2.7	10.8
After	95	239	872	2.5	9.2

As can be seen in Table 11 the module gas permeances declined by 5, 8 and 20% for N₂, O₂, and He, respectively. Although this decline is significant, the permeation properties of the used module are still within the acceptance performance range specified by CMS. Thus, we have demonstrated acceptable module stability during exposure to harsh chemicals and high temperature for about one month. Nevertheless, CMS is actively pursuing a program for improving the long term stability of a module's performance so it is acceptable for several years. This program involves the evaluation of (a) alternate potting materials, (b) heat pretreatment of the fibers, and (c) management strategies of the module during shutdowns.

Summary and conclusions of the epoxy long term test

Two epoxy brands (A and B) were evaluated as potting materials for high temperature applications in the presence of aggressive chemicals. The long term sealing capability of the epoxies was evaluated by exposing to ethanol at 120°C and 60 Psia for 369 days. This was done by measuring the leak rates of tubes partially filled with ethanol that had one end sealed with epoxy. The end of each tube was potted with either epoxy A or B and then filled with ethanol. Then the other end was capped with a fitting. After exposure to 120°C and about 60 Psia we observed that:

1. Samples made with Epoxy A leaked at a much lower rate (about 1/10) than samples with epoxy B.
2. Samples made with epoxy A seemed intact after 369 days while epoxy B samples cracked after about 100 days.

3. After the crack developed in epoxy B, the leak rate approximately doubled.
4. The ethanol leakage rate of about 0.06 mg/day (0.006%/day) in sample A was very small, and was consistent with the expected leakage rate through the fitting cap. Therefore, epoxy A seemed much better than epoxy B for high temperature operation in a chemically aggressive environment.

Details of the epoxy long term test

The experimental procedure for measuring the epoxy chemical/thermal resistance consisted of potting one end of a piece of tubing with the epoxy under evaluation and then curing. About 1 g of ethanol was added to the tube, which then had its other end capped tightly to prevent leakage. Two samples were made with epoxy A and two samples were made with epoxy B. The samples were placed in an oven at 120°C. Periodically, e.g. once a day, each sample was weighed. The sample weight vs. time was plotted and the slope determined. The slope gave the ethanol leakage rate. If the potting fails catastrophically, either because of chemical or thermal attack, the device would leak the chemicals rapidly, indicating that the epoxy is inadequate. If the rate of weight loss over the long term remained low and within the specified leakage rate of the fitting used to cap the tube, it means that the epoxy was resistant to the chemicals used at the test temperature.

The results and discussion for long term epoxy testing follow: The samples were in the oven at 120°C for 369 days. During the first 83 days the average leak rate of samples with epoxy B was almost triple the leakage rate of samples A. The leakage rate in samples A decreased after day 83 to an average rate of about 0.06 mg/day, which is about one third of the initial rate. In contrast, after day 83 the average leakage rate of samples B increased from about 0.45 to 0.95 mg/day. These data are summarized in Table 12.

Therefore, it appears that epoxy A is more suitable for long term chemical and thermal exposure than epoxy B. After four days of exposure, it was noticed that both epoxies turned dark. Otherwise, epoxy A seemed intact (see pictures 1 and 2 below). However both epoxy B samples developed cracks after about 100 days of exposure. Picture 2 shows the cracks in epoxy B after 369 days of exposure.

Table 12. Leak rate in epoxy samples exposed to ethanol at 120°C

Epoxy Sample	Ethanol leak rate (mg/day)	
	Day 1 to 83	Day 84 to 369
A1	0.18	0.048
A2	0.16	0.069
B1	0.46	0.79
B2	0.44	1.1

Picture 1. Samples of epoxy “A” after exposure to ethanol at 120°C for 369 days

Picture 2. Picture of epoxy samples “B” after exposure to ethanol at 120°C for 369 days

Task 5 High Temperature Membrane Reactor

The ultimate product from the program is a novel and energy efficient manufacturing method for MVE, though Equation (3). This ether is a building block for a number of important chemical products. Since the reaction operates at 150 to 300°C, the reaction is clearly a vapor phase reaction. The boiling point of MVE is about 5°C, and the boiling points of methanol and DMA are about 62°C. Whereas Task 3 utilizes a catalytic pervaporation membrane reactor in the liquid phase, Task 5 will require a gaseous catalytic membrane reactor. At common temperatures approaching 300°C, few membranes are suitable, and the CMS membranes are not applicable. As shown in Task 3, KSE has catalysts which can operate at lower temperatures of 125°C, but the equilibrium limitations constrain the reaction. The incorporation of the KSE catalysts into the CMS gas phase membrane systems should allow one of the first applications of catalytic membrane reactors, and will offer great energy efficiencies, due to the elimination of the high operating temperatures and the elimination of a number of distillation columns required for separation of byproducts.

Note that Equation (3) also has methanol as a product, in addition to MVE. Both MVE and methanol pass through the membrane, to drive the reaction to completion at the low temperatures. The methanol is then recycled back to the first stage reactor, providing half of the methanol requirements of Equation (2).

A total of 17 tests were performed on the vapor phase system to demonstrate the performance of the CMS-3 membrane. The membrane was operated at a feed pressure of 60 psia, and principally at an operating temperature of 125°C. A few tests were performed at lower temperatures to confirm that the selectivity was retained at lower temperatures.

Figure 11 summarizes the membrane operability and selectivity at 125°C. Note that the selectivities of all three components were determined simultaneously. The composition of the feed to the membrane system was determined by the blue bars in Figure 11, consisting of 65,000 ppm MVE, 10,000 ppm DMA, and 20,000 ppm methanol. The distribution of each component (e.g., MVE) among the feed, retentate, and permeate are shown by the various colored bars in the chart. The balance was nitrogen, at a pressure of 60 psia and a temperature of 125°C.

Note the selectivity of the membrane is evident, by examining the relative concentrations of DMA to the other two compounds. Note that DMA is largely retained by the membrane, whereas both methanol and MVE readily pass through the membrane. This selectivity is excellent, allowing the DMA to be recycled to extinction by withdrawing the reactor products from the system. The small amounts of DMA which pass through the membrane will be recycled with the methanol back to the first stage reactor feed. The MVE which passes through the membrane is produced as a product from the system. It is highly volatile, and will be readily separated from the methanol in a single stage flash column.

The selectivity of the system was also examined at low concentrations, to confirm that the selectivity is not concentration-dependent. The tests were performed at the same flow rate, temperature and pressure as the tests of Figure 11, but at the lower concentrations. These test

results are shown in Figure 12. Again, the selectivity is excellent, with the DMA being retained by the membrane, and with MVE and methanol readily passing through the membrane.

During these tests, data were also collected which were used to assess membrane permeability, and to size commercial systems. Data from one of these tests are illustrated in Table 13, showing the flow rates of feed, retentate, and permeate for the membrane.

Table 13
 Illustrative Second Stage Membrane Permeability Data
 125°C @ 60 PSIA
 CHEME51W

Feed Concentration	Inlet Flow, mL/min	Retentate Flow, mL/min	Permeate Flow, mL/min
Low	260	200	60
High	320	250	70

Extensive QA/QC tests were performed through these membrane investigations, since the membranes were being exposed to chemicals with severe solvation power, and at high temperature and pressure. The results of one of these evaluations are shown in the Table 14 below.

Table 14
Illustrative Second Stage Membrane QA/QC Data
125°C @ 60 PSIA
CHEME51W

Feed Concentration	MVE Closure	DMA Closure	Methanol Closure	Overall Closure
Low	101%	101%	102%	101%
High	86%	103%	110%	92%

In Table 14, the closure represents the percentage of the component in the feed which is accounted for in the permeate and the retentate. Ideally, of course, the recovery should be 100%, but it depends both on the accuracy of the composition measurements and the accuracy of the flow measurements. As is evident from Table 14, the experimental accuracy and consistency is excellent, whether measured as individual components or whether measured on an overall outlet/inlet mass balance.

Compositional Limits in MVE Reactor Feed -- In order to determine the composition limits for the stream entering the MVE reactor, mixtures of the four components were fed to a reactor for conversion of DMA to MVE. In this reactor, residual water can result in DMA hydrolysis to acetaldehyde and methanol. Residual methanol can result in the formation of dimethyl ether (DME) as a byproduct.

Acetaldehyde and DME yields were measured at various feed compositions to define the levels of water and methanol that can be tolerated in the second stage MVE reactor while maintaining acceptable MVE and byproduct yields.

A mixture containing a 1-to-1 molar ratio of DMA and water was fed to the MVE reactor. This represents a worst case of membrane separation, in order to define the limiting concentration. Compared to a base case with pure DMA feed, MVE yield decreased, while acetaldehyde yield increased from 1.9% to 43%. This result confirms that DMA hydrolysis occurs very rapidly at MVE synthesis conditions, and that the majority of the water must be removed prior to entering the MVE reactor.

In another experiment, a 1-to-1 weight ratio of DMA and methanol was fed to the MVE reactor. Compared to the base case with pure DMA, DME byproduct yield increased from about 1% to about 2.5%. These results suggest that, although methanol separation will still be required, the separation criteria may not be as stringent as it may be for water.

Work to define the separation performance criteria for the first membrane unit removing water, acetaldehyde, and methanol from the stream exiting the DMA synthesis reactor had continued. An equilibrium mixture of the four components prior to separation would contain about 15% acetaldehyde, 20% methanol, 55% DMA, and 10% water. Mixtures of the four components were fed to a reactor for conversion of DMA to MVE. Known potential side reactions included; (1) DMA hydrolysis to acetaldehyde and methanol, (2) formation of dimethyl ether from methanol, and (3) generation of crotonaldehyde from acetaldehyde. Byproduct yields were measured at various feed compositions and MVE reactor operating conditions to define the levels of methanol, acetaldehyde, and water that can be tolerated in the second stage MVE reactor while maintaining acceptable MVE and byproduct yields.

Earlier results showed that DMA hydrolysis occurs very rapidly at MVE synthesis conditions, and that the majority of the water must be removed prior to entering the MVE reactor. Compared to pure DMA feed, a 3-to-1 weight ratio of DMA and methanol feed to the MVE reactor increased DME byproduct yield from about 1% to about 2.5%. These results suggest that, although methanol separation may be required, the separation criteria may not be as stringent as it may be for water.

Further experiments were conducted with a 3-to-1 weight ratio feed of DMA and methanol to the MVE reactor. Systematic variation of reaction temperature and catalyst contact time in the MVE reactor was able to reduce measured DME byproduct yields to about 2.0%, but no lower. These results continue to indicate that, even with optimized MVE reactor operating conditions, methanol separation will be required in order to achieve acceptable DME byproduct yields.

In other experiments, a mixture of 15% acetaldehyde, with a 3-to-1 weight ratio blend of DMA and methanol was fed to the MVE reactor. The presence of acetaldehyde in the feed did not significantly affect the MVE product yield from DMA, but did result in the generation of about 2% crotonaldehyde byproduct. These results indicate that separation of acetaldehyde from the DMA will also be required in order to minimize crotonaldehyde byproduct generation.

Separation criteria for the first stage membrane have been defined based on the observed effects of simulated compositions leaving the first membrane unit on the selectivity performance of the second stage reactor to produce MVE from DMA via Reaction (2).

Separation criteria for this first membrane module are defined by three byproduct reactions which can occur simultaneously with Reaction (2):

- The reaction of DMA with water to form acetaldehyde and methanol. This reaction occurs extremely rapidly. The first stage membrane must be capable of achieving a water content less than 0.1% by weight in the DMA-rich stream leaving the first stage membrane.
- The reaction of methanol with itself to form dimethyl ether. Improvements in MVE synthesis catalysts achieved as part of this program have essentially eliminated dimethyl ether as a byproduct. Equilibrium limitations for Reaction (2), as well performance of the second stage membrane system, will be improved if the first stage membrane system is able to achieve a methanol content less than 25% in the DMA-rich stream leaving the first stage membrane.
- The reaction of acetaldehyde with itself to form crotonaldehyde. The first stage membrane must be capable of achieving an acetaldehyde content less than 1% by weight in the DMA-rich stream leaving the first stage membrane.

Based on these performance criteria and the known performance of the CMS membranes, detailed material balances and stream composition projections have been compiled and reviewed for both the first stage and second stage membrane systems.

Membrane Evaluation System

Because of the near-term commercial applications, KSE later utilized the DEA/EVE²⁰ synthesis in the membrane evaluation, and as a prototype system for DMA/MVE synthesis. The boiling points of DEA (102°C) and water (100°C) are extremely close, making separation by distillation exceedingly difficult. Membrane separation especially offers a highly attractive alternative for

²⁰ DEA is diethyl acetal (or 1,1-diethoxyethane); EVE is ethyl vinyl ether.

the separation of DEA and water. In addition, the overall components for the DEA system are very similar to the separation of water and ethanol, an application for which membrane separation has already been very successful.

A schematic diagram of the membrane evaluation system is shown in Figure 13. The feed tank was charged with a liquid mixture representing the expected feed composition for either the first stage membrane,

or the second stage membrane,

The liquid was metered to an evaporator, which completely vaporizes the feed stream. The vaporized feed was fed through a heated transfer line at atmospheric pressure into the shell side of the membrane module. The evaporator, transfer line, and membrane module were provided with heating media, insulation, and temperature measurement and control devices to maintain a constant temperature of about 120°C.

Retentate vapor from the membrane module was condensed in a chilled condenser at minus 10°C, and collected in the retentate receiver. Permeate vapor was withdrawn from the tube side of the membrane module under 24 to 26 inches Hg vacuum. Permeate was condensed in a chilled first stage condenser at minus 10°C, and collected in the first stage permeate receiver. Remaining overhead vapors from the first stage permeate condenser were further condensed in a cryogenic vapor trap at minus 104°C, and collected in the second stage permeate receiver.

Figure 13
Membrane Separation Evaluation System

Individual membrane evaluation runs were conducted at constant feed rate and operating conditions for the membrane module, with collection of retentate and permeate, for about 1 hour. Feed rate to the membrane module was about 20 grams per minute. After completion of a run, liquid in the retentate receiver and permeate receivers was collected, weighed, and analyzed by gas chromatography. Overall material recovery during the various membrane evaluation runs ranged from 95% to 98%. Most of the material loss was believed to be due retention of small amounts of liquid in various fittings, and on the walls of tubes and the various process equipment. The rate of residual exhaust vapors from the vacuum pump was measured with a wet test meter, and found to represent a negligible portion of the total feed rate to the process

Membrane Module Benchmark Performance Testing

A membrane module which is performing according to specification should achieve a benchmark flux ratio of helium to nitrogen of greater than 9-to-1. Prior to addition of any chemical components to the membrane module, and evaluation of membrane separation performance, the benchmark performance of the membrane module was measured with nitrogen and helium. The membrane performance with helium and nitrogen was evaluated immediately following assembly of the membrane evaluation system, and was re-evaluated at three other times during the overall evaluation program. Flux rates with helium and nitrogen were tested at feed pressures from 7 to 15 psig. Permeate gases were removed at atmospheric pressure.

Results for all benchmark tests are shown in Table 15 below. The initial benchmark test, shown in the first three rows of Table 15, was performed on the membrane module as received, and prior to exposure to any of the chemical components. Subsequent benchmark performance tests were performed on the membrane module in an “as is” state. No effort was made to dry the membrane, or otherwise remove any chemical components that may be retained within the membrane structure at the time of the test.

Table 15. Benchmark Membrane Performance Tests for Helium and Nitrogen Flux Rates

Date	Pressure, PSI	Gas Permeation Unit, Nitrogen	Flux Ratio, Helium/Nitrogen	Run Number
5/18/2009	7	83	11.3	CHEMH98W
5/18/2009	10	84	10.1	CHEMH98Y
5/18/2009	15	86	9.4	CHEMH99W
6/1/2009	7	79	7.1	CHEMI04W
6/1/2009	10	86	6.3	CHEMI04W
6/1/2009	15	88	5.6	CHEMI04W
6/11/2009	5	154	6.0	CHEMI14W
6/11/2009	7	141	5.9	CHEMI14W
6/11/2009	15	113	5.8	CHEMI14W
6/11/2009	15	118	6.4	CHEMI14W
6/16/2009	7	93	6.5	CHEMI16W
6/16/2009	15	98	6.1	CHEMI16W
6/18/2009	7	84	6.6	CHEMI18W
6/18/2009	15	104	5.4	CHEMI18W

Initial benchmark tests indicated that the membrane module as received, and prior to exposure to chemical components, was performing according to specification. Subsequent tests did not demonstrate the expected 9-to-1 flux ratio for helium and nitrogen. Discussion with CMS personnel indicated that this was likely due to benchmark testing without drying of the membrane structure.

First Stage Membrane Separation Performance Evaluation

The feed to the first stage membrane represents the expected output stream from the synthesis of DEA from acetaldehyde and ethanol by Reaction (4). The primary purpose of the first stage membrane is to remove water produced by Reaction (4), and concentrate DEA in preparation for feed to a vapor phase reactor for the synthesis of EVE from DEA. The removal of water is of primary importance, since any water present in the feed stream for EVE synthesis will result in acetaldehyde byproduct formation.

The feed mixture for the evaluation of first stage membrane separation performance represented the product from 60% conversion of acetaldehyde to DEA by Reaction (4), based on an initial molar ratio for the acetaldehyde and ethanol reactants of 2-to-1, and a reaction temperature of 20°C. The evaporator and membrane module were operated at 120°C. Permeate was removed at 26.5 inches Hg vacuum. Flow rates and compositions of the feed, retentate, and permeate streams are summarized in Table 16 below. Composition of the feed stream shown in Table 16 represents the composition as measured by GC immediately following completion of the run.

Table 16
First Stage Membrane Separation Performance
Run CHEMI17W: Single Pass Separation
Temperature: 120°C, Feed Pressure: Atmospheric
Permeate Pressure: 26.5 Inches Hg Vacuum

Stream	Rate, Grams/Minute	Acetaldehyde Composition Weight %	DEA Composition Weight %	Ethanol Composition Weight %	Water Composition Weight %
Feed	21.3	2.4	56.2	33.0	8.4
Retentate	13.9	1.9	70.8	25.3	2.0
Permeate	7.4	2.0	19.2	57.1	21.7

Retentate represented 65% of the feed stream. As shown in Table 16, water content in the retentate stream was substantially reduced, and the DEA concentration significantly increased. Acetaldehyde concentration in the retentate was also reduced.

Retentate water content, although substantially reduced in a single pass through the membrane, is still significantly above the target level. To determine if the water content could be reduced to lower levels, the retentate stream from Run CHEMI17W was collected, charged to the feed tank, and the retentate fed to the membrane module for a second membrane separation pass. Flow rate and composition results for the second pass separation are shown in Table 17.

Comparison of Table 16 and Table 17 shows that there are small compositional differences between the retentate stream from the first membrane pass, as reported in Table 16, and the feed stream for the second membrane pass, as reported in Table 17. The compositional analysis for the retentate stream shown in Table 16 was performed immediately following completion of Run CHEMI17W. This same material, reported as the feed stream for the second membrane pass in Table 17, was analyzed again immediately prior to Run CHEMI18Y. This second analysis is

reported in Table 17. The difference is likely due to a small amount of reaction which occurred during the 2-day time interval between the two analyses.

Table 17. First Stage Membrane Separation Performance
Run CHEMI18W: Second Membrane Unit in Series with Table 16 Retentate
Temperature: 120°C, Feed Pressure: Atmospheric
Permeate Pressure: 26.5 Inches Hg Vacuum

Stream	Rate, Grams/Minute	Acetaldehyde Composition Weight %	DEA Composition Weight %	Ethanol Composition Weight %	Water Composition Weight %
Feed	19.0	1.1	72.3	24.6	2.0
Retentate	12.8	0.4	84.0	14.4	1.2
Permeate	5.8	1.3	43.8	48.5	6.5

As shown by the retentate stream in Table 17, after two membrane passes, water content has been reduced from 8.4% to 1.2%, and the DEA concentration has been increased from 56% to 84%. Water clearly demonstrates the highest permeation rate, and DEA the lowest permeation rate. Both acetaldehyde content, at 0.4%, and ethanol content, at 14.4%, have achieved the membrane separation targets for these two components.

Water content, although significantly reduced from the original feed stream in Table 16, has not achieved the target level of 0.1% by weight, even after two membrane passes. Further improvement in water separation is required if the target membrane separation level for water of 0.1% by weight is to be approached.

Evaluation of Second Stage Membrane Separation Performance

The feed to the second stage membrane represents the expected output stream from the reactor for the synthesis of EVE from DEA by Reaction (5). The purpose of the second stage membrane is to provide an initial separation of EVE and DEA. It is expected that EVE will concentrate in the permeate stream, which will then be further purified by additional membrane steps. If needed, distillation will provide a final EVE product. DEA is expected to concentrate in the retentate stream, which will be recycled back to the EVE reactor.

The feed mixture for the evaluation of second stage membrane separation performance represents 30% conversion of the DEA in a DEA-rich stream to EVE by Reaction (2). The DEA-rich feed stream from the first stage membrane to the EVE reactor represents the retentate stream from a two-pass first stage membrane separation, represented by the retentate stream in Table 17. The evaporator and membrane module were operated at 120°C. Permeate was removed at 24.5 inches Hg vacuum. Flow rates and compositions of the feed, retentate, and permeate streams are summarized in Table 18 below.

Table 18. Second Stage Membrane Separation Performance
Run CHEMI19Y: Single Pass Separation
Temperature: 120°C, Feed Pressure: Atmospheric
Permeate Pressure: 24.5 Inches Hg Vacuum

Stream	Rate, Grams/Minute	Acetaldehyde Composition Weight %	DEA Composition Weight %	Ethanol Composition Weight %	EVE Composition Weight %
Feed	18.4	3.9	57.1	24.1	15.0
Retentate	13.5	2.1	66.8	15.1	16.0
Permeate	4.2	8.7	19.7	39.0	32.5

The results shown in Table 18 indicate that DEA permeates the slowest, and is concentrated in the retentate stream. Acetaldehyde appears to permeate the fastest. Ethanol and EVE appear to permeate at very similar rates.

Although the overall material balance closure for Run CHEMI19Y is greater than 96%, closure of balances for individual components is not as high. The reason for the inability to achieve complete closure on individual components is not known.

To determine whether further separation can be achieved, the retentate stream from Run CHEMI19Y was collected, charged to the feed tank, and the retentate fed to the membrane module for a second membrane separation pass. Flow rate and composition results are shown in Table 19.

Table 19. Second Stage Membrane Separation Performance
Run CHEMI21W: Second Membrane Unit in Series with Table 18 Retentate
Temperature: 120°C, Feed Pressure: Atmospheric
Permeate Pressure: 24.5 Inches Hg Vacuum

Stream	Rate, Grams/Minute	Acetaldehyde Composition Weight %	DEA Composition Weight %	Ethanol Composition Weight %	EVE Composition Weight %
Feed	18.6	2.1	66.8	15.1	16.0
Retentate	14.3	1.5	74.8	11.1	12.6
Permeate	4.0	7.4	33.7	31.3	27.5

Again, DEA is the slowest permeating component, and concentrates further in the retentate stream. Acetaldehyde appears to permeate fastest, while ethanol and EVE appear to permeate at very similar rates.

The desired end product is purified ethyl vinyl ether, EVE. The membrane did not achieve an EVE concentration greater than about 32% in either the retentate or the permeate stream. Both EVE and ethanol appear to permeate at very similar rates, suggesting that membrane separation of these two components may be very difficult. It is recommended that these results be examined, and, based on the known characteristics of the membranes, determine whether or not higher purification levels of EVE can be achieved membrane separation.

Further KSE membrane separation evaluations are recommended for future work:

- Feed streams to the second stage membrane representing DEA to EVE conversion levels up to 90% should be evaluated to see if a feed stream with a much higher EVE concentration allows for greater purification of EVE.
- The first stage membrane for water separation and DEA purification should be evaluated in liquid pervaporation mode to assess whether pervaporation may provide greater separation of water.

In summary, membrane performance evaluation may be conducted in two phases:

1. Vapor phase membrane performance evaluated with a feed stream simulating actual commercial operation.
 - a. In the first stage of the plant, the effluent from the first stage reactor feeds a first stage membrane unit. For testing the first stage membrane, a feed stream representing the actual exit composition of the DEA synthesis reactor is to be fed to the membrane module at operating conditions representative of projected commercial operation.

- i. First stage reactor tests have been completed, in which Reaction (4) converts acetaldehyde and ethanol to DEA and water. The product from this first stage reactor represents the feed to the first stage membrane unit. The reactor tests have been completed at about 100°C reactor temperature. For comparison, reactor tests have also been completed on a nitrogen-diluted mixture of the feed shown by Reaction (4), with the reactor operating at 30°C. Evaluations of catalyst activity, product yields, and reaction selectivity need to be completed in the next phase of this program.
 - ii. The future stage of the program is to evaluate the first stage membrane separation performance and operating characteristics, based on purification of the first stage reactor product. The ability of the membrane system to remove water, and provide a feed stream meeting all composition requirements to the second stage EVE reactor need to be demonstrated. These membrane tests should be performed at a temperature of about 110°C.
- b. After completion of the first stage reactor and membrane performance tests, the second stage membrane performance should also be evaluated with a feed stream representing the exit composition of an EVE synthesis reactor.
 - i. The effluent from the first stage membrane unit will be routed to a second stage reactor, in which Reaction (5) occurs.
 - ii. The product from this second stage reactor will be routed to a second stage membrane unit, to produce the EVE product and to recycle unconverted raw materials.
- 2. Additional recommendation: In the future phase of the program, membrane performance should be evaluated for the first stage membrane in liquid phase pervaporation operation. Equilibrium conversion for Reaction (4) is higher at lower temperatures, in the liquid phase. Combined reactor and membrane operation will be evaluated under liquid phase conditions at temperatures in the range of 0° C to 40° C. Permeation rates, separation performance, and membrane operating characteristics would be evaluated in liquid phase pervaporation mode. Results would be compared to gas phase operation in order to assess the operational and economic tradeoffs of vapor phase and liquid phase operation.

Task 6: Economic and Energy Analysis

The AIChE study (Vision 2020; 2000 Separation Roadmap) indicated that for a membrane reactor system to be commercially viable it must have exceptional economics, that is be able to “shut-down” existing processes and replace with new investment.⁽⁵⁾ The cost of manufacture, that is energy and material savings and increased product purity (value), has to be improved to a level to justify replacing existing facilities with the membrane reactor system. The key components in the economics are CMS membranes cost less, last longer, and have higher flux at low water activity.

There are numerous energy benefits associated with enhancing chemical reactions. The first and most direct is the energy savings by removing the water by the membrane process is significant and measured in trillions of BTU’s per year. An additional energy saving is that the same unit operation of pulling water through the membrane and leaving organics in the retentate. While we will not talk broadly about energy savings from separations we will discuss the benefits specifically related to removing water, not from a chemical reaction, but from ethanol.

The logic is the cornerstone technology in this program is rapid removal of water from an organic reaction (to enhance the reaction). This same technology can be used to separate water from ethanol to produce fuel grade ethanol. This separation therefore enhances the renewable domestic energy sources (e.g., corn) to produce fuel grade ethanol.

Energy Savings from Reactions: The energy savings from reactions relate quite extensively to the removal of water and the saving of energy in the removal of that water. This water can be removed by much more energy intensive and capital intensive azeotropic distillation processes and other related techniques. Azeotropic distillation is the most commonly used method to remove water from the reaction products. Relative to the proposed membrane dewatering method, azeotropic distillation is a much more energy intensive process because the both the water and the entrainer that is added to effect the separation are removed as vapor from the top of the column. In addition, all distillation processes require reflux in order to operate. Reflux increases the required heat input for the separation.

Based on our process models we estimate the energy savings offered by the membrane process to be approximately 100 Btu per lb of product in the manufacture of a phthalate ester with a molecular weight of 240. The energy savings per lb would be greater for lower molecular weight esters and lower for higher molecular weight esters. We consider this estimate of the energy savings to be conservative as a larger share of the market is represented by lower molecular weight esters than higher molecular weight esters. The data used as the basis of the energy savings estimate is presented in Table 20. The engineering methods employed in the calculations will not be discussed here.

Table 20
Energy Comparison of Distillation and Membrane Processes

Current Process		Membrane Reactor Process	
Phthalate Ester Production Rate (lbs/yr)	25,000,000	Production Rate (lbs/yr)	25,000,000
Xylene Latent Heat (Btu/lbmol)	15640	Xylene Use Rate (lbs/yr)	0
Xylene Use Rate (lbs/yr)	2,812,500	Water Latent Heat (Btu/lbmol)	17640
Water Latent Heat (Btu/lbmol)	17640	Water Generation Rate (lbs/yr)	1,875,000
Water Generation Rate (lbs/yr)	1,875,000	Latent Heat Energy Requirement (Btu/yr)	1,837,500,000
Latent Heat Energy Requirement (Btu/yr)	2,251,811,953	Fraction of Latent Heat Energy Recovered	0.85
Distillation Reflux Ratio	0.25	Latent Heat Energy per Unit Mass Product (Btu/lb)	11.0
Annual Column Energy Input (Btu/yr)	3,002,415,937	Water Vapor Molar Flow Rate (lbmol/hr)	11.9
Energy Use per Unit Mass Product (Btu/lb)	120	Annual Vacuum Pump Electrical Usage (Btu)	310,567,146
		Electrical Usage per Unit Product (Btu/lb)	12
		Total Energy Usage per Unit Product (Btu/lb)	23
		Energy Savings per Unit Product (Btu/lb)	97
		Fractional Energy Savings	0.80

Our focus for this program is on a membrane reactor for the manufacture of MVE. However, this is a platform technology that is applicable to a broad spectrum of equilibrium limited chemical reactions where water is an undesirable byproduct. Consequently, the target market for this process technology includes all of the chemical reaction processes listed in Table 1. The reactive distillation market opportunity is significantly smaller since reactive distillation is only useable where attractive azeotropes develop. By contrast the CMS process is useable in all equilibrium reactions where water is a product. Based on this target market, estimated at 150 million tons annual production, we estimate a total market potential energy savings of 30 trillion Btu annually or 600 trillion BTUs over 20 years. (This value is arrived at by the following calculation: 150 million tons/yr x 2000 lb/ton x 100 Btu/lb) More rigorous and conservative estimates of annual energy savings determined using the DOE on-line Chemical & Allied Processes Project Assessment Tool (CPAT) are presented Table 21 and discussed below. Our estimates of the annual energy savings for the 20 year period beginning in 2010 as well as the

cumulative energy savings are presented in Table 21. We estimate a total energy savings of 191 trillion Btu over a period of twenty years. These values were determined using the CPAT default assumptions of 30% market penetration and 20 years accelerated deployment. A projected annual target market growth rate of 2% was also assumed.

Table 21
Annual Energy Savings for 20-year period

Year	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020
Number of New Units on Line	0	578	578	577	577	577	327	327	327	326	326
Total Number of Units on Line	0	578	1156	1733	2310	2887	3214	3541	3868	4194	4520
Unit Name Plate Capacity (tons)	12500	12500	12500	12500	12500	12500	12500	12500	12500	12500	12500
Unit Startup Capacity (tons)	6250	6250	6250	6250	6250	6250	6250	6250	6250	6250	6250
Time to Name Plate Capacity (months)	6	6	6	6	6	6	6	6	6	6	6
Time to Construct Unit (months)	12	12	12	12	12	12	12	12	12	12	12
Energy Savings per Ton Product (Btu/Ton)	193298	193298	193298	193298	193298	193298	193298	193298	193298	193298	193298
Market Energy Savings for the Year (Trillion Btu)	0.0	1.0	2.4	3.8	5.2	6.6	7.6	8.4	9.1	9.9	10.7
Cumulative Market Energy Savings (Trillion Btu)	0.0	1.0	3.5	7.3	12.6	19.2	26.8	35.1	44.3	54.2	64.9

Year	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030
Number of New Units on Line	140	140	139	139	139	114	114	114	114	114
Total Number of Units on Line	4660	4800	4939	5078	5217	5331	5445	5559	5673	5787
Unit Name Plate Capacity (tons)	12500	12500	12500	12500	12500	12500	12500	12500	12500	12500
Unit Startup Capacity (tons)	6250	6250	6250	6250	6250	6250	6250	6250	6250	6250
Time to Name Plate Capacity (months)	6	6	6	6	6	6	6	6	6	6
Time to Construct Unit (months)	12	12	12	12	12	12	12	12	12	12
Energy Savings per Ton Product (Btu/Ton)	193298	193298	193298	193298	193298	193298	193298	193298	193298	193298
Market Energy Savings for the Year (Trillion Btu)	11.2	11.5	11.8	12.2	12.5	12.8	13.1	13.4	13.6	13.9
Cumulative Market Energy Savings (Trillion Btu)	76.1	87.6	99.5	111.7	124.2	137.0	150.1	163.4	177.1	191.0

Membrane Economics: KSE has completed a capital investment for MVE Manufacture for conventional plants, sized at annual MVE production of 30 and 100 million pounds. This is shown in the following Table 22.

Table 22
Capital Investment for MVE Manufacture by Conventional Plants
Cost Basis: 2005

Investment Item	Cost Factor	Conventional Technology 30 Million Annual Pounds MVE	Conventional Technology 100 Million Annual Pounds MVE
Purchased Equipment	(IPE Cost)	\$1,812,400	\$3,082,600
Installation	35% of Equip.	\$634,340	\$1,078,910
Instrumentation	10-35% of Equip	\$634,340	\$1,078,910
Piping	15-40% of Equip	\$724,960	\$1,233,040
Electrical	12-40% of Equip	\$724,960	\$1,233,040
Building Improvements	20-50% of Equip	\$906,200	\$1,541,300
Subtotal Direct Costs		\$5,437,200	\$9,247,800
Engineering & Supervision	15-20% of Directs	\$1,087,440	\$1,849,560
Construction & Fee	15-20% of Directs	\$1,087,440	\$1,849,560
Contingency	15% of Directs	\$815,580	\$1,387,170
Subtotal Indirect Costs		\$2,990,460	\$5,086,290
Fixed Capital Investment		\$8,427,660	\$14,334,090
Working Capital	15% of Fixed	\$1,264,149	\$2,150,114
Total Capital Employed		\$9,691,809	\$16,484,204

The annual operating costs for MVE manufacture by conventional plants is shown in Table 23.

Annual Operating Costs for MVE Manufacture by Conventional Plants
Cost Basis: 2005

Cost Item	Cost Factor	Conventional Technology 30 Million Annual Pounds MVE	Conventional Technology 100 Million Annual Pounds MVE
Operating Labor	0.5-4 per shift	\$640,000	\$960,000
Supervisory Labor	0.1-0.5 per shift	\$140,000	\$140,000
Maintenance	2% of Fixed	\$168,553	\$286,682
Utilities	Per Aspen IPE Design	\$5,484,150	\$18,280,500
Supplies	10% of labor	\$64,000	\$96,000
Plant Laboratory	10% of labor	\$64,000	\$96,000
Depreciation	3% of Fixed	\$280,922	\$477,803
Taxes	1% of Fixed	\$84,277	\$143,341
Insurance	1% of Fixed	\$84,277	\$143,341
Plant Overhead	50% of L+S+M	\$474,277	\$693,341
G&A	20% of L+S+M	\$189,711	\$277,336
Distribution & Selling	3% of above total	\$230,225	\$647,830
Research & Development	150% of above total	\$345,337	\$971,745
Interest	5% Capital Employed	\$484,590	\$824,210
Total Operating Cost		\$8,734,319	\$24,038,130

4. Patents: None

5. Publications / Presentations: We have presented our work at the AIChE Spring 2007 meeting in Houston in both a closed and open session. At the open session related to a broad concept of water removal there is a strong interest on the part of Baker Petrolite to collaborate with us in petroleum processing based on the platform technology associated with this program. In the closed session under DOE review we reviewed findings to date. At the meeting the following two path forward items were strongly reinforced.

- 1) Testing of separations factors in the first year and projected to 120°C is critical considering operations are at these high temperatures.
- 2) Modeling or other appropriate steps need to be taken to assure that membrane's capability to remove by-products is consistent with the reaction chemistry's ability to generate by-products.